Claims

1. Novel compounds of substituted calix(4) pyrroles namely tetraspiro cycloheptyl calix (4) pyrrole , tetraspiro cyclooctyl calix (4) pyrrole and tetraspiro (2-methyl cyclohexyl) calix(4) pyrrole as shown in structural formulae 6a, 7a and 8a of the accompanying drawings, for use in many industrial applications particularly in biological applications.
2. Novel compounds as claimed in claim 1, wherein the compounds having following properties.
   i) tetraspiro cycloheptyl calix (4) pyrrole **(6a):** ^{1}HNMR (200 MHz, $CDCl_3$): δ= 1.45-1.72 (m, 32H, cycloheptyl), 1.94-2.12 (m,16H, Cycloheptyl), 5.83 (br, d,8H, pyrrole-βH), 6.78-6.88 (br,s,4H,NH),; HR-MS (EI) for $C_{44}H_{60}N_4$: calcd: 644.4817, found: 644.4752;
   ii) tetraspiro cyclooctyl calix (4) pyrrole **(7a)**, ^{1}HNMR (200 MHz, $CDCl_3$): δ=1.18-1.82 (m, 56H, cyclooctyl), 5.93 (br,d,8H, pyrrole-βH), 6.91-6.99 (br,s,4H, pyrrole-NH); HR-MS (EI) for $C_{48}N_{68}N_4$: calcd; 700.5443, found: 700.5456; and
   iii) tetraspiro (2-methyl cyclohexyl) calix(4)pyrrole **(8a)**: HR-MS (EI) for $C_{44}H_{60}N_4$: calcd: 644.4817, found 644.4847.
3. A method for preparing substituted calix (4) pyrroles, said method comprising reacting a pyrrole with a acyclic and cyclic ketones over a mesoporus molecular sieve solid acid catalyst in presence of a solvent, at reflux temperature of about 100°C for period ranging from 10 to 72 hours, recovering the solid products by filtration, washing with deionized water and drying in air and calcined at 773K in air.
4. A method as claimed in claim 3 wherein, the catalyst is selected from MCM-41, HZSM-5 (30), Hβ, HY and SAPO-5.
5. A method as claimed in claim 3 wherein, the amount of catalyst used is ranging from 0.1 g to 1.0 g.
6. A method as claimed in claim 3 wherein, the catalysts used are having the following surface area and pore size as given below.

Catalyst	Surface area (m^2/g)	Pore size (°A)
MCM-41	980-1200	30-100
HY	525 –625	6-8
HZSM-5 (30)	275-340	5-7.5
SAPO-5	175-240	6.5-8.4
Hβ	600-680	5.5 x 6.6 to 7.5 x 8.5

7. A method as claimed in claim 3 wherein, the pore size and surface area of the catalysts used in the reaction are given in the following table.

Catalyst	Surface area (m^2/g)	Pore size (°A)
HY	593	7.3
HZSM-5 (30)	310	5.6
SAPO-5	207	7.4
Hβ	640	6.5 x 7.6

8. A method as claimed in claim 3 wherein, the solvent used for refluxing is selected from dichloromethane, methanol, and acetonitrile.
9. A method as claimed in claim 3 wherein, the molar ratio of pyrrole to ketone is selected in between 1:1 to 1:4.
10. A method as claimed in claim 3 wherein, the cycloketone is selected from the group comprising cyclohexanone, cycloheptanone, cyclopentanone and cyclooctanone.
11. A method as claimed in claim 3 wherein acyclic ketone is selected from the group comprising methyl ethyl ketone and 3-pentanone.
12. A method as claimed in claim 3 wherein, acyclic products are obtained using the catalyst HY.
13. A method as claimed in claim 3 wherein, major amounts of liner products are obtained using catalyst HZSM-5 (30).
14. A method as claimed in claim 3 wherein, the yield of the calix (4) pyrrole is up to 70%.

15. A method as claimed in claim 3 wherein, the selectivity of the calix (4) pyrrole is up to 90%.
16. A method as claimed in claim 3 wherein, the calix (4) pyrrole obtained are:
    i) octamethyl calix (4) pyrrole **(1a)**;
    ii) Tetraethyl Tetra methyl calix (4) pyrrole **(2a)**;
    iii) octaethyl calix (4) pyrrole **(3a)**;
    iv) tetraspiro cyclohexyl calix (4) pyrrole **(4a)**;
    v) tetraspiro cyclopentyl calix (4) pyrrole **(5a)**;
    vi) tetraspiro cycloheptyl calix (4) pyrrole **(6a)**,
    vii) tetraspiro cyclooctyl calix (4) pyrrole **(7a)**;
    viii) (2-methyl cyclohexyl) calix (4) pyrrole **(8a)** and
    ix) dimer, trimer and tetramers of pyrroles
17. A method for preparing calix (4) pyrroles or tetraspiro calix (4) pyrroles, said method comprising mixing a pyrrole with a acyclic or cyclic ketones over a molecular sieve solid acid catalyst and subjecting the mixture to microwave radiation for 3 to 10 minutes and optionally, refluxing using a solvent for extracting the compounds.
18. A method as claimed in claim 17 wherein, the solvent used for refluxing is selected from dichloromethane, methanol, and acetonitrile.
19. A method as claimed in claim 17 wherein, the molar ratio of pyrrole to ketone is 1:1.
20. A method as claimed in claim 17 wherein, in the reaction of equimolar ratio of pyrrole and cyclohexanone, dichloromethane is used as a solvent for refluxing to obtain cyclic products.
21. A method as claimed in claim 17 wherein, the catalyst used is mesoporus molecular sieve catalyst (MCM-41).
22. A method as claimed in claim 17 wherein, the mesoporus catalyst used in the reaction is having surface area ranging between 980 –1200 m^2/g.
23. A method as claimed in claim 17 wherein, the mesoporus catalyst used in the reaction is having pore size ranging between 30- 100°A.
24. A method as claimed in claim 17 wherein, the microwave heating is carried out for a period ranging from 2 minutes to 15 minutes, more preferably 3 to 10 minutes.

25. A method as claimed in claim 17 wherein, the microwave radiation level is at about 2450 MHz.
26. A method as claimed in claim 17 wherein, the acyclic ketone used is acetone.
27. A method as claimed in claim 17 wherein, the cyclic ketone used is cyclohexanone.
28. A method as claimed in claim 17 wherein, the preparation of calix (4) pyrroles or tetraspiro calix (4) pyrroles is a solvent free process.
29. A method as claimed in claim 17 wherein, the calix (4) pyrrole obtained are:
    i) octamethyl calix (4) pyrrole **(1a)**;
    ii) Tetraethyl Tetra methyl calix (4) pyrrole **(2a)**;
    iii) octaethyl calix (4) pyrrole **(3a)**;
    iv) tetraspiro cyclohexyl calix (4) pyrrole **(4a)**;
    v) tetraspiro cyclopentyl calix (4) pyrrole **(5a)**;
    vi) tetraspiro cycloheptyl calix (4) pyrrole **(6a)**,
    vii) tetraspiro cyclooctyl calix (4) pyrrole **(7a)**;
    viii) (2-methyl cyclohexyl) calix (4) pyrrole **(8a)**; and
    ix) dimer, trimer and tetramers of pyrroles